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NATIONAL WATER QUALITY NETWORK APPLICATIONS AND DEVELOPMENT REPORT. 6. EVALUATION OF THE FIELD PERFORMANCE OF A HAYS DISSOLVED OXYGEN ANALYZER

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Public Health Service
Cincinnati, Ohio

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SUMMARY

The Hays Dissolved Oxygen Analyzer was operated at the Little Miami River Field Test Station of the National Water Quality Network from July 17, 1962, to September 27, 1962. This evaluation was undertaken in order to determine if the instrument is suitable for utilization in the National Water Quality Network's field activities.

The instrument yielded oxygen concentration values which in average deviated by 0.15 ppm from the oxygen concentration of the influent water. Percent saturation errors varied with the saturation value of the sample and indicate the necessity for a recalibration of the percent saturation circuit. The instrument was capable of recording temperature with an average deviation of 0.19°C.

Throughout the period of this evaluation, no lost time may be charged against the Hays Analyzer. However, some time was lost due to failure of auxiliary equipment.

In the opinion of the writer the Hays Analyzer is suitable for field application. Its application is limited, however, by initial and operating costs, weight, size, and required maintenance by high level personnel. The analyzer is not compatible with the integrated systems approach now being developed by the National Water Quality Network in cooperation with several instrument manufacturers.

INTRODUCTION

The National Water Quality Network is interested in the testing and application of instrumentation to the measurement and recording of water quality parameters. A parameter of major importance is dissolved oxygen.

There are three methods of instrumentally measuring dissolved oxygen available at this time. These involve (a) polarographic, (b) conductometric, and (c) partial pressure techniques.

The polarographic method was tested as a portion of another study and will be reported on separately.

The conductometric method with its requirement of deionized water is limited to either waters of extremely low mineral content or short term studies. For these reasons, this method is not considered applicable to long-term continuous sampling of surface waters.

The objective of this study was to evaluate the field performance of a dissolved oxygen analyzer operating on the partial pressure principle and to investigate the factors which affect its performance.

The analyzer evaluated was a production model manufactured by the Hays Corporation of Michigan City, Indiana. The theoretical principles, and the methodology underlying the dissolved oxygen analyzer were originally developed at the Robert A. Taft Sanitary Engineering Center. 1/ 2/

1/ Levine, H. S., and Walker, W. W. American Chemical Society, 1955.

2/ Levine, H. S., and Kleinschmidt, R. S. Public Health Service, DHEW.

LOCATION OF TEST

This study was conducted in the National Water Quality Network's Field Test Station on the Little Miami River at Cincinnati, Ohio.

This station is equipped with both a jet and a submersible pump. The intake to ejector piping on the jet pump was 1-1/4 inch diameter and 1-1/2 inch diameter from ejector to pump. The return line from pump to ejector was 1-1/4 inch in diameter. The submersible pump was installed with a one-inch diameter pipe line. Polyethylene pipe was used in both systems. The total length of each of these lines was 400 feet. The lift from river to pump manifold is 44 feet.

A rudimentary laboratory was set up at the station so that bench analyses of dissolved oxygen could be made quickly as required in the field by the azide-modified Winkler method. Reagents and standard solutions were provided by the National Water Quality Network's Service Laboratory.

DESCRIPTION OF ANALYZER

GENERAL: The Hays Dissolved Oxygen Analyzer records the temperature of the water and dissolved oxygen content in either parts per million or percent saturation. The temperature is detected by a thermistor in the analyzer's incoming water line.

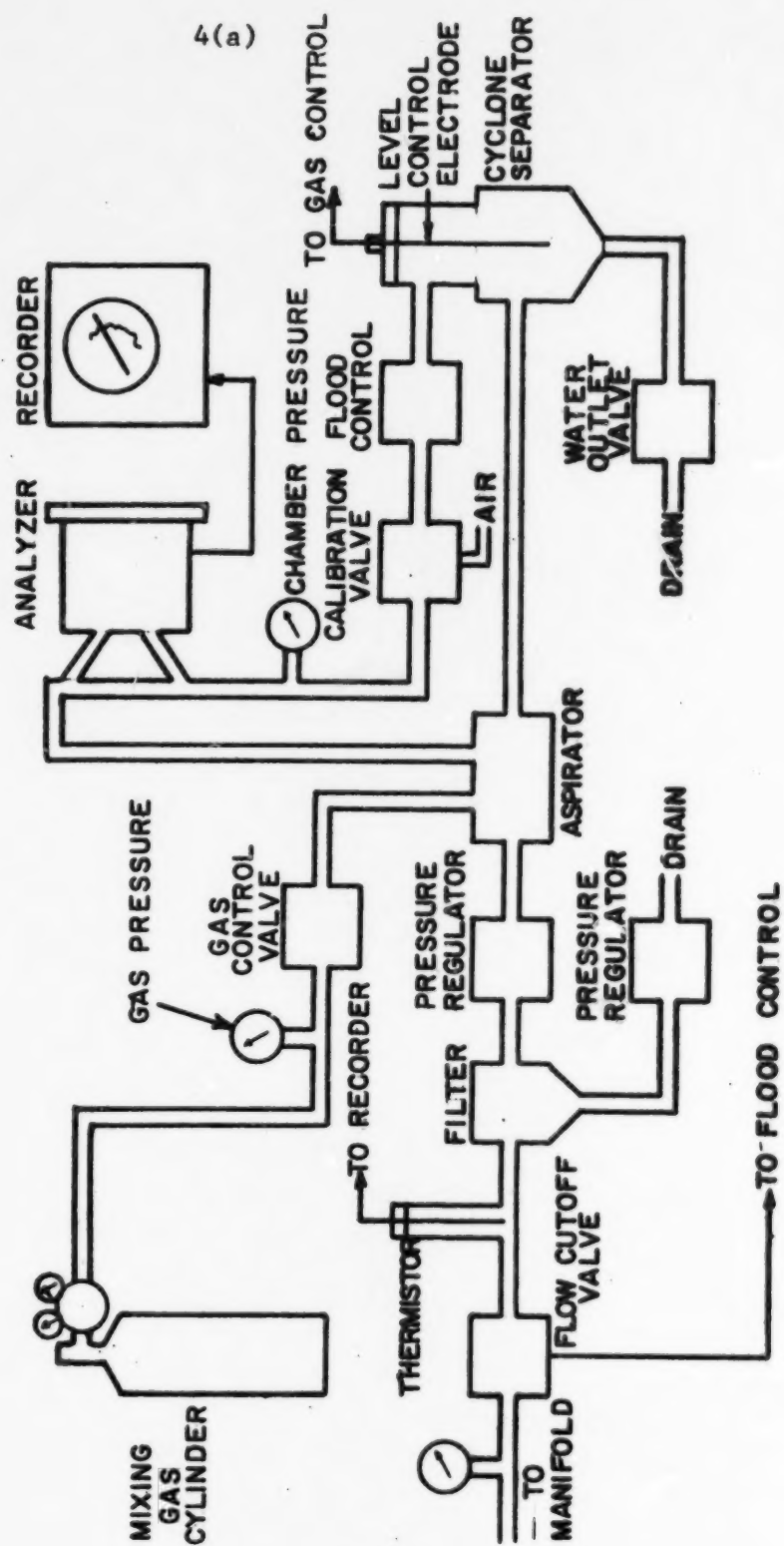
Conversion of oxygen content in ppm to percent saturation is accomplished by a thermistor located in the cyclone separator, Figure 1. This thermistor corrects the oxygen content for the temperature of the water. The selection of operating mode (ppm or percent saturation) is controlled by a switch on the front of the recorder case.

The Hays Analyzer uses a chart calibrated from 0-15 units with 0.3 unit being the width of the finest division. The range for parts per million concentration is 0 to 15. Temperature range is 0-30°C. This requires that the recorded temperature values be multiplied by two. The range of percent saturation is 0-150%. Thus, the chart reading must be multiplied by 10.

This chart scale calibration limits the readability of parts per million of dissolved oxygen to 0.1, saturation to 1%, and temperature to 0.2°C. Readings to a greater degree of precision are limited by the width of the pen trace.

Red ink was used in the oxygen recording pen and green in the temperature recording pen.

FIGURE 1 SCHEMATIC DIAGRAM OF HAYS DISSOLVED OXYGEN ANALYZER



THEORETICAL: The Hays Dissolved Oxygen Analyzer operates on Henry's Law which states "the quantity of gas which dissolves in a solvent at a given temperature is directly proportional to the partial pressure of that gas."

Henry's Law is limited to those cases where the gas does not react chemically with the solvent. The oxygen-water system obeys Henry's Law.

In the Hays Analyzer nitrogen gas is injected into the water sample, mixed, and then the oxygen-nitrogen gas mixture is stripped from the water solution. The gas mixture is fed into the analyzer cell and then is recycled back to the aspirator unit. The gas system comprises a closed loop which insures that equilibrium is reached between the dissolved oxygen in the water and the oxygen gas in the loop. Since this loop has a volume, there is a definite time required for the system to respond to a change in the dissolved oxygen content of the influent sample. The time required for the system to reach 90% of a sudden change is termed the response time and for the instrument used was about 3.5 seconds.

The schematic diagram of the Hays Analyzer has been shown in Figure 1. The performance of each sub-unit will be discussed under operational description.

PHYSICAL: The analyzer consists of two major units. These are the recorder and its associated amplifiers and the magnetic analyzer unit. On the back of the magnetic analyzer unit are mounted the gas control system, water control valves, cyclone separator and incidental piping and tubing. The recorder weighs about 60 pounds and the magnetic analyzer unit weighs about 100 pounds. These sub-assemblies are mounted in a house which measures 2.25 feet wide, 4.89 feet high, and 3.10 feet deep. The overall volume is 33.7 cubic feet. Inside the house are the electrical distribution lines, sample pipes, and pressure gages. Space was provided for installing the nitrogen gas cylinder inside the house. The housing used in this study was deeper than required since space was available for the installation of an automatic data logging device. This device was not used in this study.

The overall weight of this unit complete with a large gas cylinder is estimated at 400 pounds.

A floor area of 4.0 feet by 5.5 feet should be provided for this instrument to allow the doors to be fully opened and for water and drain connections to be made. Future designs of housing should place some of the control valves and gages at the front of the instrument to permit ready control of the system variables.

COMPONENTS: The Hays Dissolved Oxygen Analyzer is a complex of many components and systems. For example, there are electronic amplifiers, motors, fluid pressure regulators and gas control valves. There are hydraulic, gas and electrical systems within the analyzer. The following discussion will be limited to those units which have a bearing upon the operation and necessary theory.

Amplifiers: Two identical amplifiers were used in the Hays Analyzer. One was in the temperature channel and the other was in the oxygen channel. These amplifiers had a gain control which was found to be quite sensitive. At one setting the gain was insufficient and with just a little more gain an over-sensitive condition prevailed. When such a system is in an over-sensitive condition, it is subject to "hunting" which is a violent searching for the correct re-balance point. Once the optimum gain was obtained, however, there was little or no drift in the setting.

Control Valve: This valve controls the flow rate through the analyzer. It can be fully opened to permit an uninhibited discharge of water. When it is closed, water flows through a 1/8-inch diameter hole in the valve gate. In operation, this valve is fully closed and it is opened only for standardizing the analyzer.

Filter: Before the water enters the analyzer, it passes through a Cuno edge-type filter which has brass plates spaced to 0.020 inches. This will take out only large particles and leave the smaller particles to pass through. No flow stoppages occurred during this study as a result of particulate matter clogging the water lines, valves, or filter.

Gas Control Valves: This unit, which is actuated by the level control electrode consists of two solenoid valves in series. No operational difficulty was traceable to its operation.

Analyzer Cell: This component operates on the paramagnetic properties of oxygen. It consists of two chambers in which are mounted two matched thermistors. One chamber is under a very intense magnetic field. The chambers and thermistors are heated. In operation, a mixture of nitrogen and oxygen enters the analyzer, and oxygen is attracted to the chamber which lies in the magnetic field. The oxygen becomes heated, loses its paramagnetism, and is swept out of the cell by incoming cooler paramagnetic oxygen. Since nitrogen is non-magnetic, equal flow rates of this gas exist in each chamber. Thus the thermistor in the magnetic field is preferentially cooled by an amount proportional to the oxygen content of the sample. Its resistance changes are measured by a self-balancing Wheatstone bridge circuit and applied through an amplifier to a chart.

Level Control: The water level in the cyclone separator is maintained fairly constant by use of controlled gas flow. When the water level in the separator rises, contact is established between the separator case and the level control electrode. This signal controls the solenoid valves which permit nitrogen gas to enter the system. The incoming gas forces down the level in the separator until contact is broken at which time the gas flow ceases.

The solenoid valve should be actuated from two to six times per minute in normal operation. The frequency of actuation is a function of the differential of the incoming gas pressure over the chamber pressure. The

normal operating differential is 1/2 to 1 psig. In this evaluation study, the chamber pressure was maintained at 3.0 psig and the nitrogen gas pressure was 3.5 psig. As the pressure differential is increased, the frequency of actuation is decreased. This causes the recorded valves to "cycle" or wander back and forth over the correct value. The amplitude of this wandering has approached ± 0.15 ppm at 12 ppm. Reducing the gas pressure to allow more frequent actuation reduces the cycling. There is no one optimum setting which will produce cycle free recording over a wide range of dissolved oxygen concentrations. This is particularly noticeable when the saturation exceeds one-hundred percent.

Initially, a single stage regulator was used to drop the gas pressure from about 2000 psig in the tank to 3.5 psig in the analyzer. This was a very critical setting and changed as the tank temperature changed. Later, a two stage regulator was installed, and found capable of maintaining a constant output pressure with changes in temperature.

The dissolved oxygen analyzer as delivered had a three-inch long level control electrode. Knight (3/) has reported frequent flooding with this length of electrode. Throughout the period of this study a five-inch electrode was used and no routine flooding was experienced.

3/ Knight, W. E., personal communication to M. B. Ettinger, 1962.

Flood Control: Under certain conditions, it is possible for water to be forced out of the top of the cyclone separator and to enter the oxygen-nitrogen gas loop where it could damage the thermistors in the analyzer cell. In order to prevent such an occurrence, a flood control device has been installed on the analyzer. This device consists of a conductivity cell installed in the gas loop. When water reaches this cell, a relay system closes a solenoid valve which cuts off the flow of water into the instrument.

The conditions under which flooding can occur are (a) an obstruction in the analyzer water drain; (b) an empty gas cylinder; (c) an obstruction in the gas input line (d) a dirty or corroded water level electrode.

Two flooding events occurred during this study. One was caused by a leaking pressure regulator on the nitrogen tank which exhausted the gas supply and the other event was traced to a blocked nitrogen gas line. The line was blocked by dirt introduced by the change-over from one nitrogen tank to another. It is felt that these lost-time periods are chargeable to the auxiliary equipment and not to any design or construction detail of the Hays Analyzer.

TEST PROCEDURE

Before this study began, all electronic components were tested to insure peak performance. The instrument received a complete inspection for any worn items which may have required replacement. The lubrication procedure was followed in order to place the mechanical systems in the best operating condition.

A warm-up period of 24 hours was allowed before water was introduced into the instrument. A warm-up of four hours is required to stabilize the temperature in the analyzer cell compartment. This extended warm-up was used as a short-term life test of the electronic equipment. After this warm-up period, the temperature channel was adjusted to record the temperature of the manifold which was determined by a conventional partial immersion laboratory thermometer inserted into the manifold by-pass.

Following the adjustment of the temperature channel, the water pressure relief valve on the manifold was adjusted until a pressure of 50 psig was maintained at the analyzer input. Next, the gas pressure regulator was adjusted until 3.5 psi was indicated on the gas feed line gage. The water line pressure regulators were then adjusted until the chamber pressure gage read three pounds per square inch.

The instrument was then standardized and zeroed by procedures specified in the maintenance manual. Water samples were collected at the manifold and analyzed using the Winkler method as described in the National Water Quality Network's Operating Manual. The analytical results were compared with the recorded values. The manifold concentration is based upon a single determina-

tion rather than the average of repetitive determinations. At each sampling, temperature, concentration and percent saturation were read from the Hays Analyzer. Temperature and concentration were determined at the manifold and theoretical percent saturation computed.

The instrument was operated for ten days on the submersible pump and for ten days on the jet pump. These periods do not include weekends, holidays and other periods when the instrument was in operation but no sampling was in progress. The instrument was in an "on" condition from July 17 to September 27, 1962, and no failure of its operating components occurred.

RESULTS AND DISCUSSION OF RESULTS

The Hays Analyzer was tested for its ability to record dissolved oxygen concentration, oxygen percent saturation, and temperature, accurately. Pipe and pumps may have an effect upon the dissolved oxygen. For this reason, the Hays Analyzer results will be compared against the results obtained from samples collected at the manifold rather than collected in the river.

Oxygen Concentration: The Hays Analyzer was operated principally as an oxygen concentration recorder. This mode was selected because prior knowledge indicated that the Little Miami River was quite likely to exceed 150% saturation but not likely to exceed a 15 ppm concentration. Secondly, the analytical method determined oxygen concentration and not saturation.

During this study, eighty-one comparisons were made between the manifold concentration and the recorded result. These data are tabulated in Tables 1 and 2 and are presented graphically in Figure 2. Overall, the Hays Analyzer had a mean absolute deviation of 0.15 ppm, a mean absolute deviation of 0.13 ppm on water supplied by the submersible pump and a mean absolute deviation of 0.16 ppm on water delivered by the jet pump. (Table 3). The oxygen concentration delivered to the Hays ranged from 1.4 ppm to 11.8 ppm with the jet pump and from 5.2 ppm to 13.1 ppm with the submersible pump. The deviations listed in Tables 1 and 2 were further refined by computing the algebraic mean deviation. (Table 4). If the deviations were randomly distributed, a value of zero for the algebraic deviation

TABLE #1

Hays-Manifold Comparison Data
Chronological sequence of dissolved oxygen concentrations
Submersible Pump

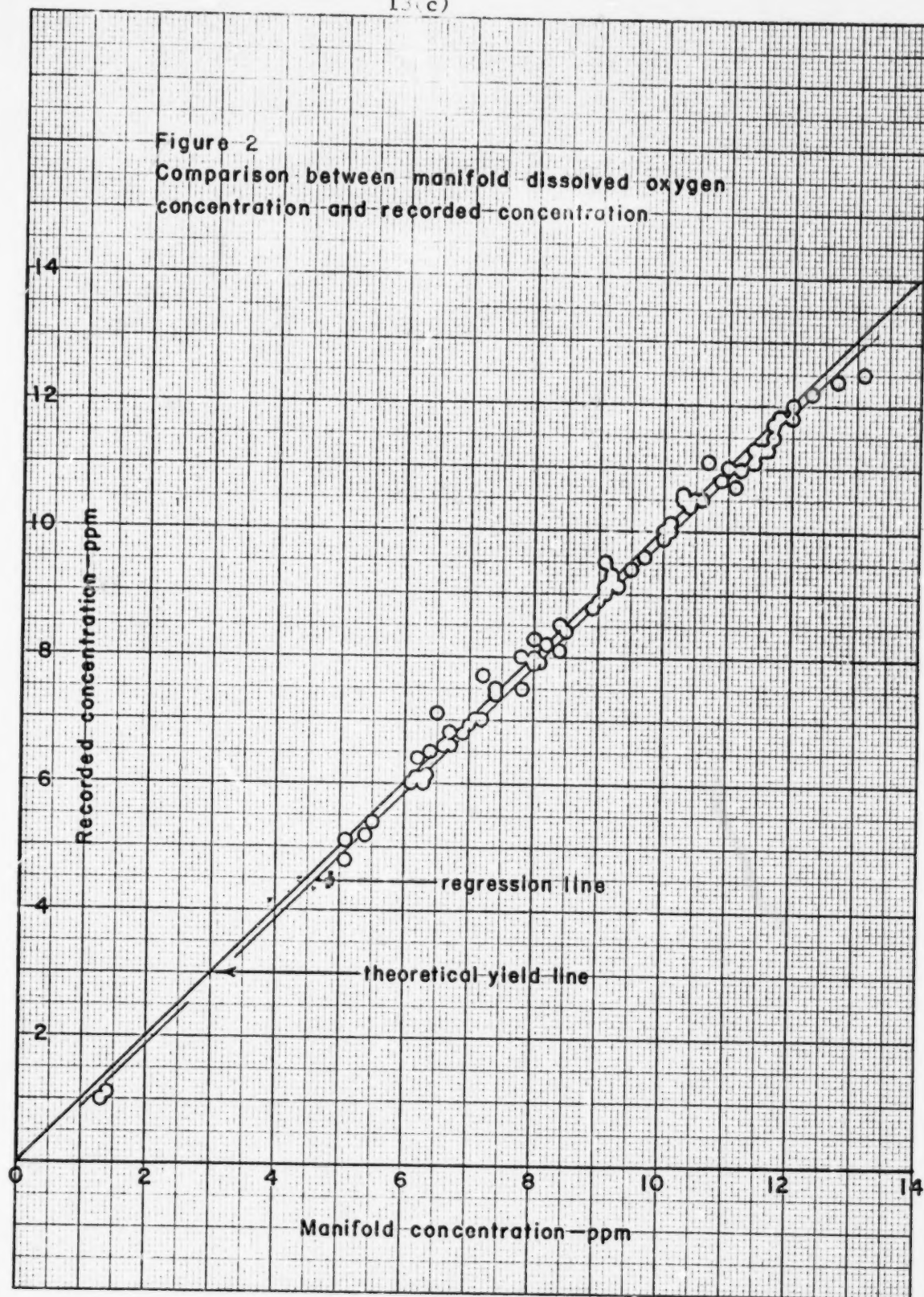
Date 1962	Manifold ppm	Hays ppm	Deviation ppm	Date 1962	Manifold ppm	Hays ppm	Deviation ppm
7/26	9.2	9.3	-0.1	8/16	10.6	10.5	+0.1
7/27	7.4	7.4	0.0	8/16	11.5	11.3	+0.2
7/27	8.0	8.0	0.0	8/17	8.0	7.9	+0.1
7/27	8.9	8.8	+0.1	8/17	9.1	9.0	+0.1
7/27	10.5	10.5	0.0	8/17	10.1	10.1	0.0
7/27	11.0	11.0	0.0	8/17	11.4	11.3	+0.1
7/28	12.0	11.8	+0.2	8/17	11.7	11.7	0.0
7/28	12.7	12.4	+0.3	8/17	12.0	12.0	0.0
7/28	13.1	12.5	+0.6	8/17	12.3	12.2	+0.1
8/10	10.3	10.5	-0.2				
8/13	6.2	6.4	-0.2				
8/13	6.5	7.1	-0.6				
8/13	7.2	7.7	-0.5				
8/13	9.5	9.4	+0.1				
8/14	6.4	6.5	-0.1				
8/14	7.0	6.9	+0.1				
8/14	8.0	7.9	+0.1				
8/14	8.4	8.5	-0.1				
8/14	8.9	8.8	+0.1				
8/15	7.1	7.0	+0.1				
8/15	8.4	8.5	-0.1				
8/15	9.1	9.5	-0.4				
8/15	10.0	10.0	0.0				
8/15	10.4	10.4	0.0				
8/16	7.4	7.4	0.0				
8/16	8.5	8.4	+0.1				
8/16	9.2	9.2	0.0				

TABLE #2

Hays-Manifold Comparison Data
Chronological sequence of dissolved oxygen concentration
Jet Pump

Date 1962	Manifold ppm	Hays ppm	Deviation ppm	Date 1962	Manifold ppm	Hays ppm	Deviation ppm
8/27	9.5	9.4	+0.1	9/17	6.6	6.6	0.0
8/27	10.9	10.8	+0.1	7/17	7.8	8.0	-0.2
8/28	6.7	6.6	+0.1	9/18	5.5	5.4	+0.1
8/28	7.4	7.4	0.0	9/18	6.1	6.0	+0.1
8/28	9.0	8.9	+0.1	9/18	7.4	7.5	-0.1
8/28	11.2	11.0	+0.2	9/18	8.2	8.2	0.0
8/28	11.7	11.5	+0.2	9/18	9.1	9.1	0.0
8/29	9.3	9.1	+0.2	9/18	10.1	10.1	+0.1
8/29	10.0	9.9	+0.1	9/19	6.9	6.8	+0.1
8/29	11.4	11.1	+0.3	9/19	6.7	6.8	-0.1
8/29	11.6	11.3	+0.3	9/20	6.6	6.6	0.0
8/30	7.2	7.0	+0.2	9/20	6.3	6.1	+0.2
8/30	7.8	7.5	+0.3	9/20	8.1	7.9	+0.2
8/30	8.4	8.1	+0.3	9/20	10.3	10.6	-0.3
8/30	8.9	8.8	+0.1	9/20	9.7	9.6	+0.1
9/30	11.1	10.7	+0.4	9/21	7.0	6.9	+0.1
8/31	6.3	6.0	+0.3	9/31	8.0	8.3	-0.3
8/31	6.2	6.1	+0.1	9/21	8.4	8.5	-0.1
8/31	6.7	6.7	0.0				
8/31	1.4	1.1	+0.3				
8/31	5.1	4.8	+0.3				
9/13	1.3	1.0	+0.3				
9/13	5.4	5.2	+0.2				
9/13	7.4	7.4	0.0				
9/13	10.7	11.1	-0.4				
9/13	11.8	11.8	0.0				
9/17	5.10	5.1	0.0				

Figure 2
Comparison between manifold dissolved oxygen
concentration and recorded concentration



13(d)

TABLE #3

Hays-Manifold Comparison
 Analysis of deviations, absolute values

Deviation (x)	Jet		Subs.		Total	
	f	fx	f	fx	f	fx
0.0 ppm	9	0.0	11	0.0	20	0.0
0.1	16	1.6	16	1.6	32	3.2
0.2	8	1.6	4	0.8	12	2.4
0.3	10	3.0	1	0.3	11	3.3
0.4	2	0.8	1	0.4	3	1.2
0.5	0	0.0	1	0.5	1	0.5
0.6	0	0	2	1.2	2	1.2
Totals	45	7.0	36	4.8	81	11.8
Mean deviation, ppm	0.156		0.133		0.146	

TABLE #4

Hays-Manifold Comparison
Analysis of deviations, algebraic values

Deviations ppm (x)	Jet			Submersible				Total			
	Negative		Positive	Negative		Positive	fx	Negative		Positive	fx
	f	fx	f	f	fx	f		f	fx	f	
0.0	0	0.0	9	0	0	11	0	0	0.0	20	0.0
0.1	3	0.3	13	4	0.4	12	1.2	7	0.7	25	2.5
0.2	1	0.2	7	2	0.4	2	0.4	3	0.6	9	1.8
0.3	2	0.6	8	0	0	1	0.3	2	0.6	9	2.7
0.4	1	0.4	1	1	0.4	0	0.0	2	0.8	1	0.4
0.5				1	0.5	0	0.0	1	0.5	0	0.0
0.6				1	0.6	1	0.6	1	0.6	1	0.6
Totals	7	1.5	38	9	2.3	27	2.5	16	3.8	65	8.0
Residual fx		+4.0				+0.2				+4.2	
Total		45				36				81	
Deviation, ppm		+0.089				+0.006				+0.052	

would indicate equal weighting above and below the regression line. The algebraic mean deviations are +0.052 ppm, +0.006 and +0.089 ppm for the total population, submersible and jet pump waters, respectively. From the sign convention used, a positive value indicates that the manifold concentration is higher than the recorded concentration. The small value of the algebraic mean shows that the Hays Analyzer is nearly free of a bias in its recording. If a bias exists then the Hays is under-recording the correct concentration by a small amount, by an average algebraic deviation of 0.052 ppm for a large number of samples.

The deviations between the Hays Analyzer results and the results determined at the manifold ranged from +0.6 to -0.6 ppm with a mean absolute deviation of 0.15 ppm. The standard deviation of the deviations is ± 0.19 ppm, Table 5. This standard deviation is strongly affected by the extreme values. There is evidence presented in the original data sufficient to reject the following deviations: +0.6, -0.6, -0.5, and -0.4 ppm. If these values are dropped from consideration, the mean absolute deviation, total population, computes to 0.13 ppm. Retaining the questionable data places a more severe test upon the Hays Analyzer. For this reason these data will be retained in this study.

Applying statistical theory to the values computed above, the Hays Analyzer should produce data with an average deviation of 0.15 ppm from the concentration of water supplied. In the future 68.3% of the observations should be within a range of deviations of -0.14 to +0.24 ppm; 95.4% would be within a range of -0.33 to +0.43 ppm, and 99.7% of the data would be within the range -0.52 to +0.62 ppm.

TABLE #5

Total Hays-Manifold Comparisons
Computation of standard deviation

Hays-Manifold Deviation ppm (d)	Frequency (f)	fd	Deviation From Mean (x)	x ²	fx ²
-0.6	1	-0.6	-0.652	0.425,104	0.425,104
-0.5	1	-0.5	-0.552	0.304,704	0.304,704
-0.4	2	-0.8	-0.452	0.204,304	0.408,608
-0.3	2	-0.6	-0.352	0.123,904	0.247,808
-0.2	3	-0.6	-0.252	0.063,504	0.190,512
-0.1	7	-0.7	-0.152	0.023,104	0.161,728
0.0	20	0.0	-0.052	0.002,704	0.054,080
+0.1	25	+2.5	+0.048	0.002,304	0.057,600
+0.2	9	+1.8	+0.148	0.021,904	0.197,136
+0.3	9	+2.7	+0.248	0.061,504	0.553,536
+0.4	1	+0.4	+0.348	0.121,104	0.121,104
+0.5	0	0.0	+0.448	0.200,704	0.000,000
+0.6	1	+0.6	+0.548	0.300,304	0.300,304
Totals	81	+4.2			3.022,224

$$d \text{ mean} = \frac{4.2}{81} = 0.052 \text{ ppm}$$

$$x = d - d \text{ mean}$$

$$s = \sqrt{\frac{\sum f(x)^2}{n-1}} = \sqrt{\frac{3.022,224}{80}} = .0377778$$

$$= \pm 0.19 \text{ ppm}$$

Percent Saturation: The Hays Dissolved Oxygen Analyzer is capable of presenting the dissolved oxygen content in terms of percent saturation. The conversion from parts per million to percent saturation is made by a thermistor located in the body of the cyclone separator. This thermistor corrects the oxygen concentration for the solubility of oxygen at the sample temperature.

In this study, 65 comparisons of manifold and records data were obtained. From these data, a percent saturation values was computed using the solubility figures in Steel. ^{4/} This data is repeated for convenience in Table 6. The observed and computed values are listed in Table 7.

The computed values of saturation ranged from 16 to 149 percent; while the recorded values ranged from 9 to 149 percent. There were 10 events of the recorder reading off-scale and these are not included in the above 65 comparisons. From the plotting in Figure 3, there appears to be a drift in the data, particularly at the higher values of percent saturation. The differences in percent saturation, Column 7, Table 7, were then plotted against manifold theoretical percent saturation, in Figure 4. This figure shows that the differences are lowest in the vicinity of 70-percent saturation and highest near 125-percent saturation. Since the Hays Analyzer has proven capable of yielding accurate concentration and temperature values, it must be concluded that these departures are inherent to the percent saturation thermistor or its circuitry. Other workers have reported

^{4/} Steel, E. W. Water Supply and Sewerage.

15(a)

TABLE #6

Solubility of Oxygen
In Fresh Water

Temperature °C	Dissolved Oxygen ppm	Temperature °C	Dissolved Oxygen ppm
0	14.62	16	9.95
1	14.23	17	9.74
2	13.84	18	9.54
3	13.48	19	9.35
4	13.13	20	9.17
5	12.80	21	8.99
6	12.48	22	8.83
7	12.17	23	8.68
8	11.87	24	8.53
9	11.59	25	8.38
10	11.33	26	8.22
11	11.08	27	8.07
12	10.83	28	7.92
13	10.60	29	7.77
14	10.37	30	7.63
15	10.15		

Source: Steel, Ernest W., "Water Supply and
Sewerage", Second Edition, 1947.
McGraw Hill, New York, 1947, P. 483.

TABLE #7

Percent Saturation Tabulation and Computation

Date 1962	Manifold Dissolved Oxygen ppm	Manifold- Temperature °C	Theoretical Manifold Oxygen Content at Saturation ppm	Theoretical Manifold Percent Saturation	Hays Percent Saturation	Difference Manifold PS - Hays PS
7/26	9.3	24.6	8.44	110	119	-9
7/27	7.4	21.0	8.99	82	87	-5
7/27	8.0	22.6	8.74	92	97	-5
7/27	10.5	25.0	8.38	125	144	-19
8/13	6.5	25.2	8.35	78	89	-11
8/13	7.2	25.4	8.32	86	97	-11
8/13	9.5	26.8	8.10	117	125	-8
8/14	6.4	23.0	8.68	74	77	-3
8/14	7.0	22.9	8.70	80	84	-4
8/14	8.0	23.1	8.66	92	95	-3
8/14	8.4	23.0	8.68	97	103	-6
8/14	8.9	23.0	8.68	102	105	-3
8/15	7.1	21.2	8.96	79	81	-2
8/15	8.4	24.0	8.53	98	105	-7
8/15	9.1	25.1	8.36	109	122	-13
8/15	10.0	25.3	8.33	120	132	-12
8/15	10.4	25.8	8.25	126	145	-19
8/16	7.4	22.8	8.71	85	89	-4
8/16	8.4	25.3	8.33	101	108	-7
8/16	9.2	26.0	8.22	112	120	-8
8/16	10.6	26.2	8.19	129	145	-16
8/16	11.5	26.3	8.18	141	off scale	--
8/17	8.0	24.2	8.50	94	98	-4
8/17	9.1	25.2	8.35	109	116	-7
8/17	10.1	26.2	8.19	123	136	-13
8/17	11.4	26.4	8.16	140	off scale	--
8/17	11.7	26.2	8.19	143	off scale	--
8/17	12.0	26.2	8.19	147	off scale	--
8/17	12.2	26.2	8.18	149	off scale	--
8/27	9.5	25.4	8.32	114	123	-9

15(b) Contd.

TABLE #7 (Contd)

Percent Saturation Tabulation and Computation

Date 1962	Manifold Dissolved Oxygen ppm	Manifold Temperature °C	Theoretical Manifold Oxygen Content at Saturation ppm	Theoretical Manifold Percent Saturation	Hays Percent Saturation	Difference Manifold PS - Hays PS
8/27	10.9	26.0	8.22	133	148	-15
8/28	6.7	24.6	8.44	79	82	-3
8/28	7.4	25.0	8.38	88	92	-4
8/28	9.0	25.2	8.35	108	114	-6
8/28	11.2	26.2	8.19	137	off scale	--
8/28	11.7	26.5	8.14	144	off scale	--
8/29	9.3	26.2	8.19	115	121	-6
8/29	10.0	26.8	8.10	123	134	-11
8/29	11.4	27.0	8.07	141	off scale	--
8/29	11.6	27.0	8.07	144	off scale	--
8/30	7.2	25.4	8.32	85	89	-4
8/30	7.8	26.0	8.22	95	97	-2
8/30	8.4	26.1	8.20	102	104	-2
8/30	8.9	27.0	8.07	110	117	-7
8/30	11.1	27.4	8.01	139	149	-10
8/31	6.3	25.8	8.25	76	75	+1
8/31	6.2	26.0	8.22	75	76	-1
8/31	6.7	25.8	8.25	81	88	-7
8/31	1.4	26.0	8.22	17	14	+3
8/31	5.1	26.2	8.19	62	60	+2
9/13	1.3	25.2	8.35	16	9	+7
9/13	5.4	24.4	8.47	64	61	+3
9/13	7.4	24.4	8.47	87	90	-3
9/13	10.7	24.8	8.41	128	147	-19
9/13	11.8	25.2	8.35	141	off scale	--
9/17	5.1	23.8	8.56	60	62	-2
9/17	6.6	24.1	8.52	78	80	-2

TABLE #7 (Contd)

Percent Saturation Tabulation and Computation

Date 1962	Manifold Dissolved Oxygen ppm	Manifold Temperature °C	Theoretical Manifold Oxygen Content at Saturation ppm	Theoretical Manifold Percent Saturation	Hays Percent Saturation	Difference Manifold PS - Hays PS
9/17	7.8	24.6	8.44	92	100	-8
9/18	5.5	22.7	8.72	63	64	-1
9/18	6.1	23.0	8.68	70	71	-1
9/18	7.4	23.0	8.68	85	91	-6
9/18	8.2	23.4	8.62	95	101	-6
9/18	9.1	23.8	8.56	106	114	-8
9/18	10.1	23.6	8.59	118	126	-8
9/19	6.9	22.0	8.83	78	80	-2
9/19	6.7	22.0	8.83	76	79	-3
9/20	6.6	20.5	9.08	73	75	-2
9/20	6.3	20.8	9.03	70	70	0
9/20	7.9	21.0	8.99	88	92	-4
9/20	10.3	21.0	8.99	115	126	-11
9/20	9.7	21.0	8.99	108	114	-6
9/21	6.9	20.0	9.17	75	79	-4
9/21	8.0	20.0	9.17	87	90	-3
9/21	8.4	19.8	9.20	91	96	-5

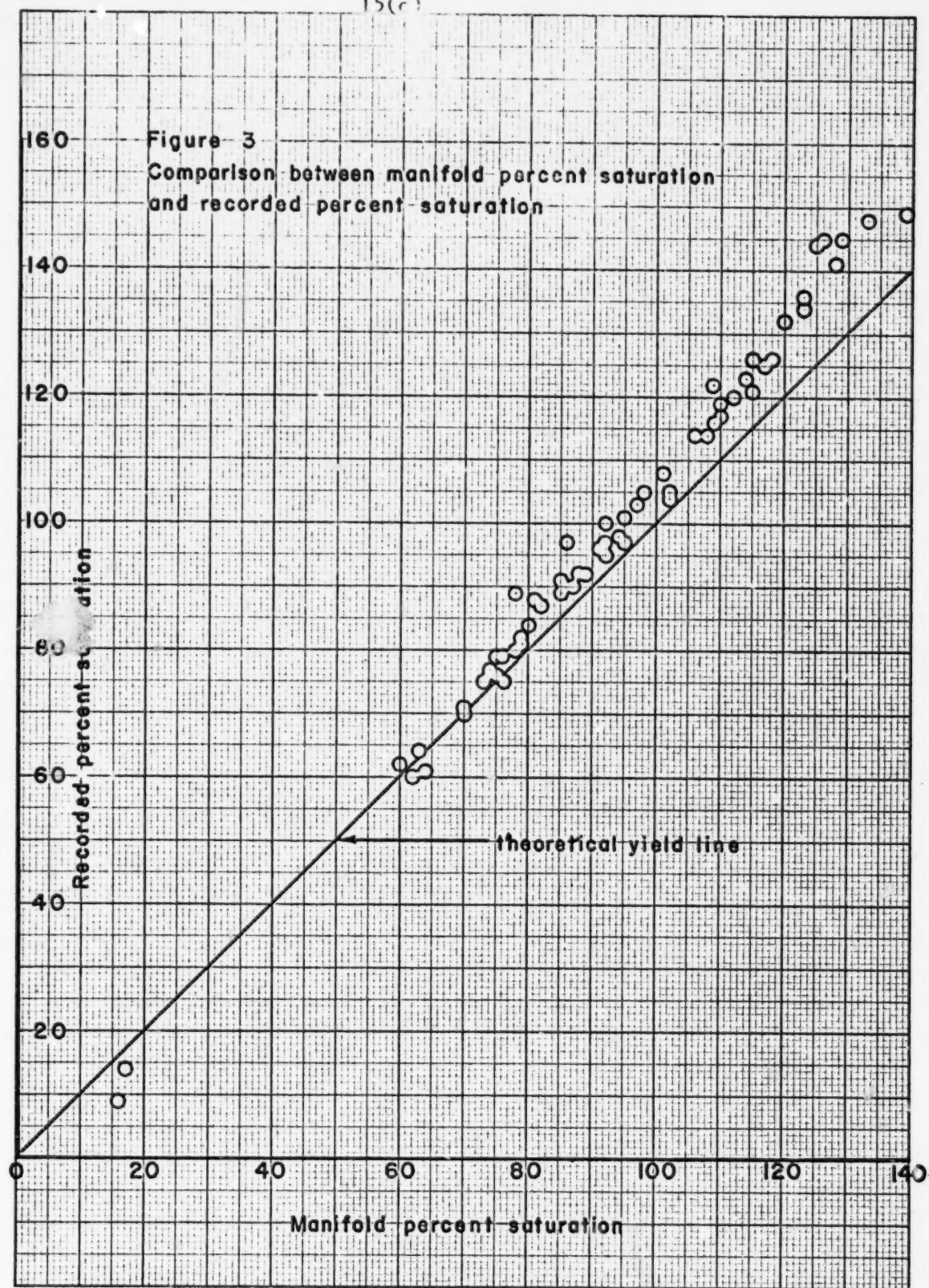
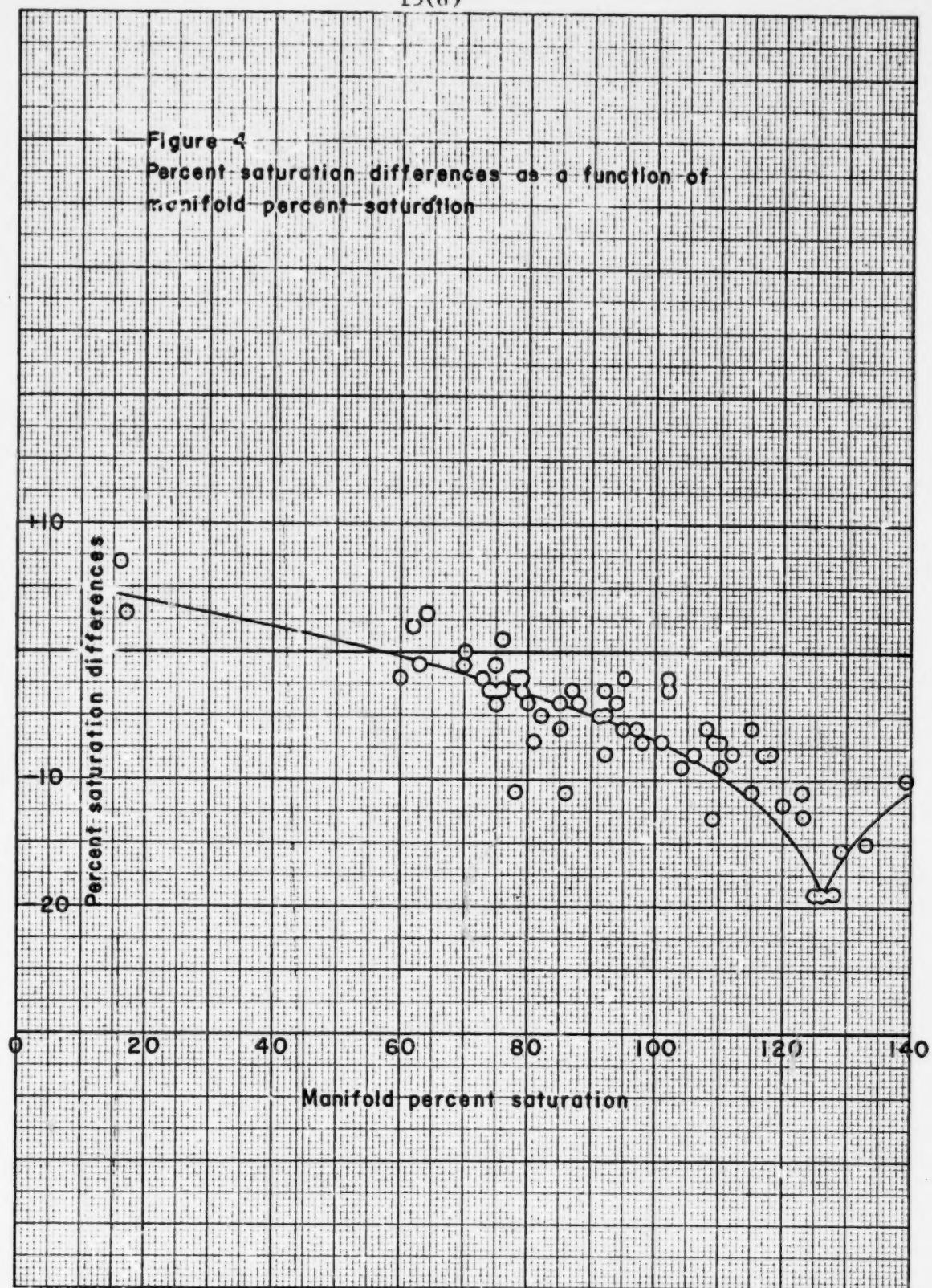


Figure 4
Percent saturation differences as a function of
manifold percent saturation



that the instrument is capable of giving values of percent saturation accurate to $\pm 2\%$ over its range. ^{5/}

To investigate the normal range of percent saturation errors taken from a recorder, consider the following case:

Temperature values accurate to $\pm 0.2^\circ\text{C}$.

Dissolved oxygen concentrations accurate to $\pm 0.15^\circ\text{C}$.

Saturated water at 25°C is being sampled.

The computations are shown in the following:

	D.O. Error -0.15 ppm		No D. O. Error		D.O. Error +0.15 ppm	
Error in temperature= +0.2°C	8.23 8.36	25.2 98.4	8.38 8.36	25.2 100.2	8.53 8.36	25.2 102.0
No temperature error	8.23 8.38	25.0 98.2	8.38 8.38	25.0 100.0	8.53 8.38	25.0 101.8
Error in temperature= -0.2°C	8.23 8.40	24.8 98.0	8.38 8.40	24.8 99.8	8.53 8.40	24.8 101.6

LEGEND:

A	B
C	D

A = Concentration of D.O. in ppm.

B = Temperature in $^\circ\text{C}$.

C = Saturation D.O. at temperature B.

D = Percent saturation of B & C.

From this square it can be shown that the worst error incidental to normal operation is $\pm 2.0\%$. An error in temperature at 25°C of $\pm 0.2^\circ\text{C}$ gives rise to errors in saturation of $\pm 0.2\%$ for constant concentration. If the temperature is constant and the dissolved oxygen varies by ± 0.15 ppm, an error of $\pm 1.8\%$ saturation arises. The square shows that the worst conditions arise when the errors are both plus or both minus for temperature and concentration, respectively. The erratic performance of this instrument should be further investigated to see if a faulty adjustment or component exists somewhere in the circuitry.

^{5/} Levine, H. S., and Kleinschmidt, Principles and Problems in Development of the SEC Dissolved Oxygen Analyzer.

Thermometry: One parameter recorded by the Hays Dissolved Oxygen Analyzer is temperature. This is a necessary measurement if dissolved oxygen concentrations are to be converted to percent saturation.

A total of 68 observations of manifold and recorder temperatures were made over a range of 19.8 to 28.0°C at the manifold. These data are tabulated in Table 8. The recorder deviated +0.6 to -0.5°C from the manifold reading, with a mean absolute deviation of 0.185°C and an algebraic deviation of +0.065°C, Table 9. It should be stressed that no insulation existed on the copper pipe which fed water from the manifold to the instrument. The chart calibration and multiplication factor of two would give rise to errors of $\pm 0.2^\circ\text{C}$ for a $\pm 0.1^\circ\text{C}$ chart reading error.

Since the computed mean absolute deviation falls within the anticipated deviation, it is concluded that this system is performing satisfactorily.

Gas Consumption: In normal operation this instrument consumed enough nitrogen gas to cause the tank pressure to fall by an average of 17 psi per day. This is an inexact value since the tank pressure is affected by temperature variations, and the test station temperature varied over wide limits. If a drop of 17 psi per day is allowed, a 220 cubic foot tank with an initial pressure of 2300 psi should last 135 days or about 4-1/2 months. This agrees with the manufacturer's statement that such a tank should last several months. It must be recognized that the gas consumption rate will increase with lower value of dissolved oxygen and for a different station may vary from these figures obtained on the Little Miami River.

17(a)

TABLE #8

Chronological Sequence
of Observed Temperatures

Date 1962	Manifold Temperature °C	Recorded Temperature °C	Deviation °C
7/20	25.0	24.6	+0.4
7/23	25.0	25.4	+0.6
7/24	23.0	22.6	+0.4
7/24	23.4	23.4	0.0
7/24	24.4	24.6	-0.2
7/25	26.5	26.8	-0.3
7/26	23.3	23.4	-0.1
7/26	24.8	24.8	0.0
7/27	21.0	20.8	+0.2
7/27	22.3	22.4	-0.1
7/28	25.8	25.8	0.0
8/10	27.9	28.0	-0.1
8/13	25.0	24.8	+0.2
8/14	23.0	22.8	+0.2
8/14	22.9	23.0	-0.1
8/14	23.1	23.0	+0.1
8/14	23.1	23.1	0.0
8/15	21.8	21.2	+0.6
8/15	24.0	23.8	+0.2
8/15	25.1	25.0	+0.1
8/15	25.3	25.8	-0.5
8/15	25.8	25.8	0.0
8/16	23.0	22.8	+0.2
8/16	25.3	25.2	+0.1
8/16	26.0	26.0	0.0
8/16	26.2	26.4	-0.2
8/16	26.3	26.4	-0.1
8/17	24.2	24.0	+0.2
8/17	25.2	25.4	-0.2
8/17	26.2	26.4	-0.2
8/17	26.4	26.2	+0.2
8/17	26.2	26.4	-0.2
8/17	26.2	26.4	-0.2
8/17	26.3	26.4	-0.1
8/27	25.4	25.6	-0.2
8/27	26.0	26.2	-0.2
8/28	24.9	24.6	+0.3
8/28	25.0	24.6	+0.4
8/28	25.2	25.2	0.0

17(a) Contd.

TABLE #8 (Contd.)

Chronological Sequence
of Observed Temperatures

Date 1962	Manifold Temperature °C	Recorded Temperature °C	Deviation °C
8/28	26.2	26.2	0.0
8/28	26.5	26.4	+0.1
8/29	26.2	26.2	0.0
8/29	26.8	26.6	+0.2
8/29	27.0	26.8	+0.2
8/29	27.0	26.9	+0.1
8/30	25.4	25.4	0.0
8/30	25.8	26.0	-0.2
8/30	26.0	26.1	-0.1
8/30	27.0	27.0	0.0
8/31	26.0	25.8	+0.2
9/17	23.8	23.6	+0.2
9/17	24.1	23.6	+0.5
9/17	24.6	25.0	-0.4
9/18	22.7	22.4	+0.3
9/18	23.0	22.8	+0.2
9/18	23.0	22.8	+0.2
9/18	23.4	23.4	0.0
9/18	23.8	23.6	+0.2
9/18	23.6	23.6	0.0
9/19	22.0	22.2	-0.2
9/20	20.5	20.2	+0.3
9/20	20.8	20.6	+0.2
9/20	21.0	20.4	+0.6
9/20	21.0	21.0	0.0
9/20	21.0	21.0	0.0
9/21	20.0	20.2	-0.2
9/21	20.0	19.6	+0.4
9/21	19.8	19.6	+0.2

17(b)

TABLE #9

Computation of Absolute and
Algebraic Temperature Deviations

Deviation °C	Frequency (f)	fd
d		
-0.5	1	-0.5
-0.4	1	-0.4
-0.3	1	-0.3
-0.2	11	-2.2
-0.1	7	-0.7
0.0	15	0.0
+0.1	5	+0.5
+0.2	16	+3.2
+0.3	3	+0.9
+0.4	4	+1.6
+0.5	1	+0.5
+0.6	3	1.8
	<u>68</u>	

Absolute total = 12.6

Absolute mean deviation = $12.6 \div 68 = 0.185^{\circ}\text{C}$

Algebraic total = +4.4

Algebraic mean deviation = $4.4 \div 68 = +0.065^{\circ}\text{C}$

Required Purge Time: The standardization procedure requires that atmospheric air be introduced into the analyzer cells through the calibration valve. The instrument is then adjusted to an oxygen saturation value computed from temperature, barometric pressure and humidity readings.

Opening the gas loop in this manner effectively contaminates the system. It was of interest to establish the minimum time, following standardization, that reliable dissolved oxygen concentrations could be read. This time has been termed "purge time". It is a measure of the time necessary for the oxygen in the gas loop to reach equilibrium with the oxygen dissolved in the influent water.

On July 27, 1962, the instrument was standardized and placed in a running condition. Readings were taken at intervals following standardization and were plotted. The tabulated data is in Table 10, and the plot is in Figure 5. From the plot in Figure 5, it can be seen that a time interval of one hour following standardization must be allowed for purging.

The standardization procedure requires from 10 to 30 minutes depending upon the amount of adjustment required. A routine service visit would then require from 70 to 90 minutes to standardize the analyzer and to insure that it was indicating the correct dissolved oxygen concentration after purging.

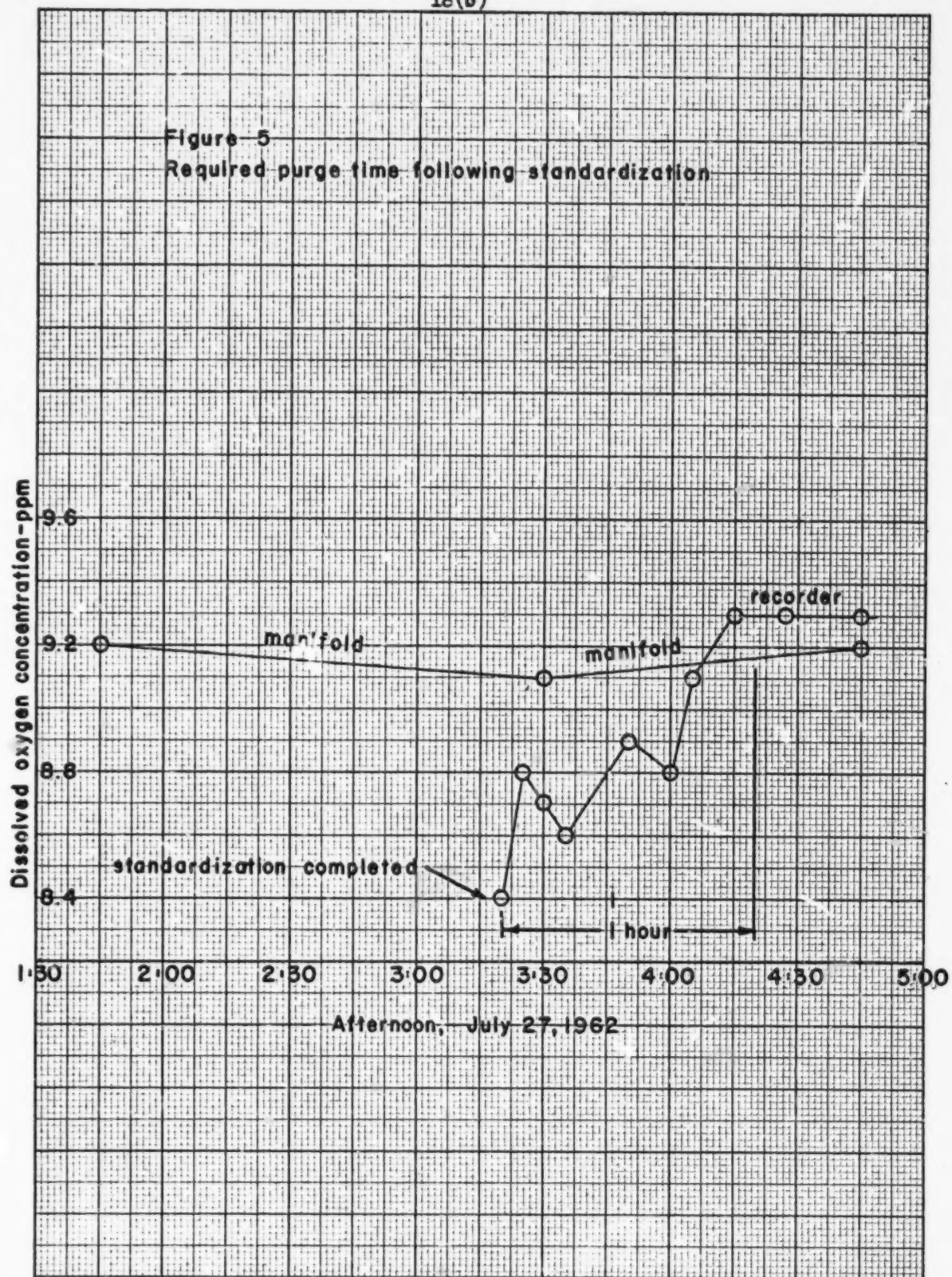
18(a)

TABLE #10

Required Purge Time Data

Time 7/27/62	Hays Dissolved Oxygen ppm	Remarks
1:45 pm	--	Manifold dissolved oxygen 9.2 ppm Standardization completed
3:20 pm	8.4	
3:25 pm	8.8	Manifold dissolved oxygen 9.1 ppm
3:30 pm	8.7	
3:35 pm	8.6	
3:50 pm	8.9	
4:00 pm	8.8	
4:05 pm	9.1	
4:15 pm	9.3	
4:27 pm	9.3	Manifold dissolved oxygen 9.2 ppm
4:45 pm	9.3	

Figure 5
Required purge time following standardization



BIBLIOGRAPHY

Dixon, William S.--"Pollution Control By Continuous Dissolved Oxygen Analysis and Associated Instruments", P. 153. Proceedings of the 1960 Seminar on Water Quality Measurement and Instrumentation, U.S. Department of Health, Education and Welfare 1961.

Levine, H. S., and Walker, W. W.--"The Continuous Measurement and Recording of Dissolved Oxygen in Water, Part 1, Theoretical Basis", presented at 127 American Chemical Society Meeting, April 9, 1955.

Levine, H. S., and Kleinschmidt--"Principles and Problems in Development of the S.E.C. Dissolved Oxygen Analyzer", U.S. Department of Health, Education and Welfare.

Steel, Ernest W.--"Water Supply and Sewerage", Third Edition, McGraw Hill, New York, N.Y., 1947.

Knight, W. E.--"Operation of a Hays D.O. Analyzer", June 27, 1962. Personal communication to Mr. M. B. Ettinger.

Hays Corporation Maintenance Manual.--The Hays Corporation, Michigan City, Indiana.